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WICHITA STATE UNIV KS DEPT OF CHEMISTRY  
MODEL STUDIES OF ENERGETIC COMPOUNDS.(U)

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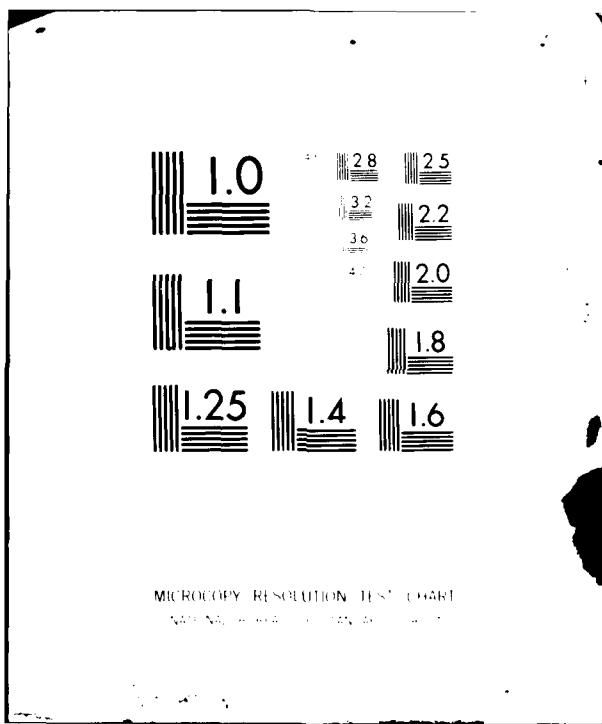
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MODEL STUDIES OF ENERGETIC COMPOUNDS.

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## MODEL STUDIES OF ENERGETIC COMPOUNDS

### I. Objectives:

A. Long Range. Chemical explosives have been used as weapons for centuries, however, systematic physical and chemical studies of energetic materials have been carried out only since World War II. Even then, we still do not have a detailed knowledge of the exact species in the reaction zone or the applicable kinetic and reaction products of a detonation.

Modern weapons are exposed to ever increasing severe environments such as aerodynamic heating and high shock pulses of extended duration in the msec range. Energetic materials capable of surviving this environment and functioning properly must be developed at a reasonable cost. Consequently, research is needed in thermal decomposition kinetics to understand the initiation process.

In order to provide necessary shelf-life of energetic materials, we must develop the knowledge to predict the aging process of energetic materials under ambient conditions. This requires research in room temperature kinetics, and how the aging mechanism is affected by binders, etc. Models are needed for the interaction of energetic materials with non-energetic materials at ambient environmental conditions.

Non-ideal energetic materials show a strong potential for sizeable gains in performance, based on a more efficient use of the available energy. However, before this concept can be applied to specific systems, a more detailed understanding of the non-ideal explosive behavior must be acquired. This necessitates research in the following areas: (1) effects

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of molecular weights on reaction products, (2) identification and quantification of reaction products, (3) reaction kinetics and controlling factors, (4) determination of the state of the reaction products and (5) mathematical modeling of the non-ideal detonation phenomena.

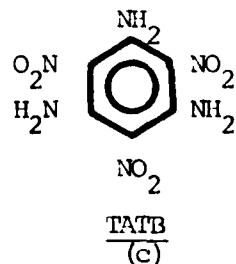
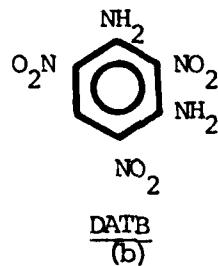
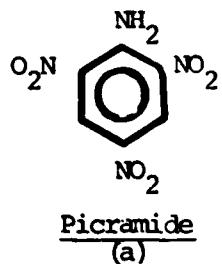
B. Immediate. The initial objectives of this study included the following: (1) Determination of the mode of thermal decomposition of DATB (diaminotrinitrobenzene-DATNB) and TATB (triaminotrinitrobenzene-TATNB), and the identification of the molecular species produced. (2) Evaluation of the induction periods and energies of activation associated with the thermal decomposition of DATB and TATB. (3) Determination of binder properties of TNB (trinitrobenzene) by studying the DATB-TNB and TATB-TNB molecular complexes by stop-flow and static UV methods.

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## II. Research Project Status:

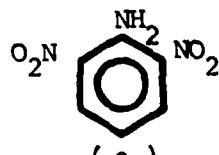
A. Mode of Thermal Decomposition of Picramide and DATB. In this study of energetic compounds, it was necessary to substitute picramide (a) for TATB (c) due to the temperature range limitation of the available EPR spectrometer. In particular, it was impossible to obtain temperatures above 280°C with any degree of accuracy. Thermal studies of TATB require 320°C or above. Consequently, picramide was an obvious substitute as the first compound in this series of energetic materials. Highly purified picramide melts at 194°C and therefore, its thermal decomposition properties are readily monitored by the available EPR spectrometer system.



The thermal decomposition of a variety of energetic materials is often facilitated by the presence of binding agents and various impurities left behind during the chemical synthesis of the energetic material. We have observed this in the cases of TNT, RDX, HMX and other compounds which were thermally decomposed in the microwave cavity of an EPR spectrometer. This is a typical result for free radical reactions whose progress is enhanced by the presence of paramagnetic impurities.

In view of the above, it was necessary to purify both picramide and DATB such that their melting points were narrowly defined. This was accomplished by multiple recrystallizations from benzene and ethanol.

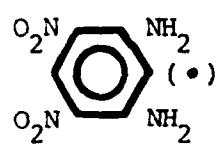
The next problem was the determination of a suitable medium or host matrix for the energetic material. Two such materials were deemed suitable. These were hexamethyl benzene, a low melting solid, and diethyl adipate, a high boiling ether. Typical EPR spectra of radical intermediates produced in the thermal decomposition of picramide and DATB are given in figures 1 and 2. These data were analyzed to give the hyperfine coupling constants associated with the proposed radical species, a' and b'.



(a')

$$2a_{\text{H}} = 5.70 \text{ gauss}$$

$$2a_{\text{N}} = 2.85 \text{ gauss}$$



(b')

$$5a_{\text{H}} = 2.67 \text{ gauss}$$

$$2a_{\text{N}} = 10.75 \text{ gauss}$$

These results are consistent with the loss of  $\text{NO}_2$  as is the case with the thermal decomposition of TNT, RDX and HMX. Simulated EPR spectra of a' and b' are given in figures 3 and 4 which were produced using the EPR spectra simulation program of Goldberg.

The EPR hyperfine coupling constants are assigned to the nitro group nitrogens on the basis of (a) theoretical calculations using MNDO UHF methods (see Table I) (b) experimental results obtained by previous investigators and (c) a limited choice in the case of a'. A similar rationale was used to assign the hydrogen hyperfine splitting constants to the ring hydrogen atoms.

TABLE I: EPR HYPERFINE CONSTANTS

Calculated vs. experimental hyperfine coupling constants (gauss) for the picramide anion and radical species a' and b', respectively.

<u>Hyperfine Constant</u>	<u>Picramide Anion</u>	
	<u>Experimental</u>	<u>Calculated</u>
$a_N(\text{NO}_2)$	3.72	0.9
$a_N(\text{NH}_2)$	0.41	0.7
$a_H(\text{meta})$	7.02	17.3
$a_H(\text{para})$	1.76	11.7
$a_H(\text{NH}_2)$	0.41	1.0
<u>Radical Species a'</u>		
$a_N(\text{NO}_2)$	2.85	0.4
$a_N(\text{NH}_2)$	1.0	4.5
$a_H(\text{meta})$	5.70	10.7
$a_H(\text{NH}_2)$	1.0	0.5
<u>Radical Species b'</u>		
$a_N(\text{NO}_2)$	10.75	0.8
$a_N(\text{NH}_2)$	1.0	0.6
$a_H(\text{para})$	2.67	6.2
$a_H(\text{NH}_2)$	2.67	0.5

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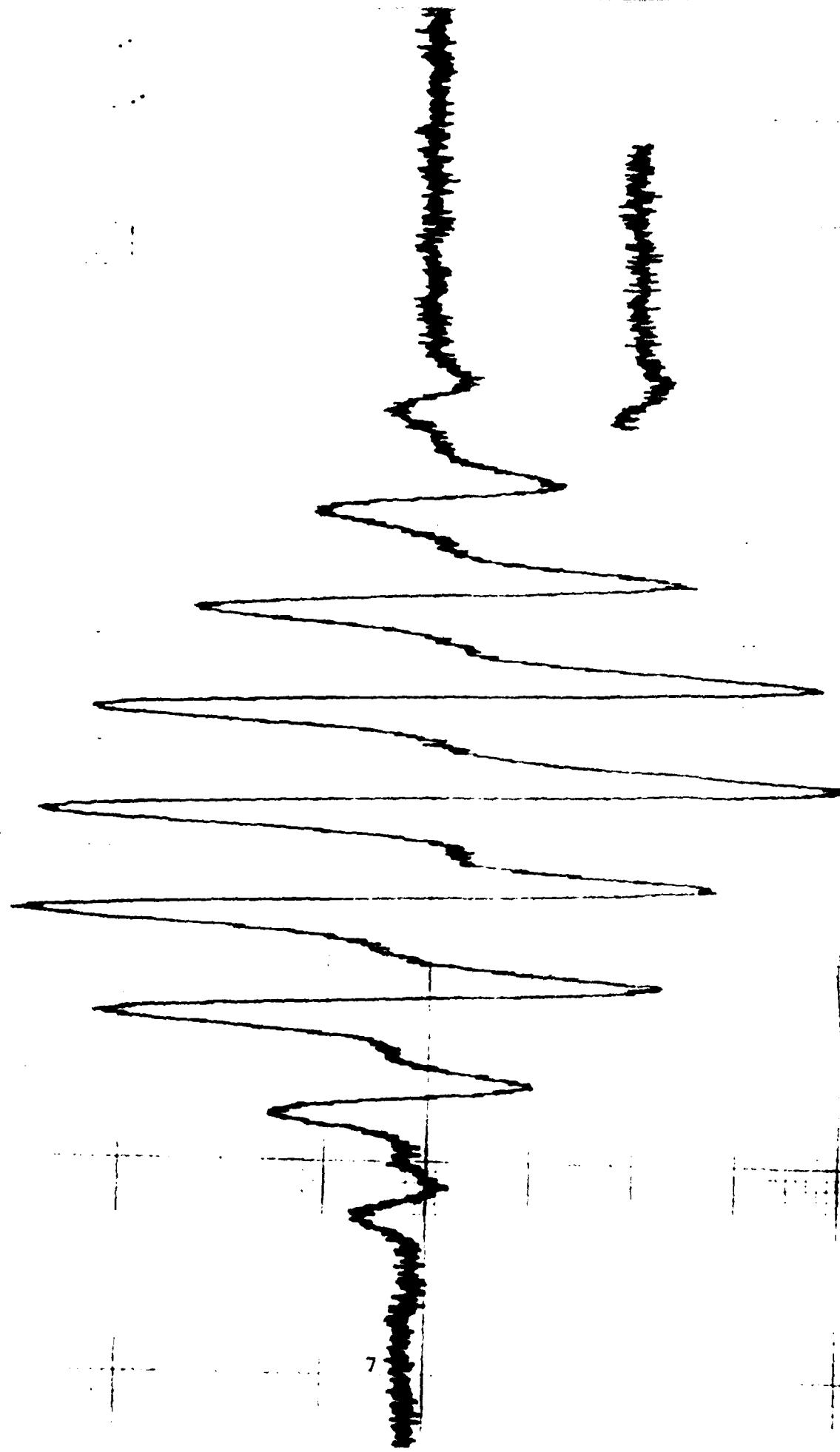


Figure 1: EPR Spectrum of Picramide Radical (a')

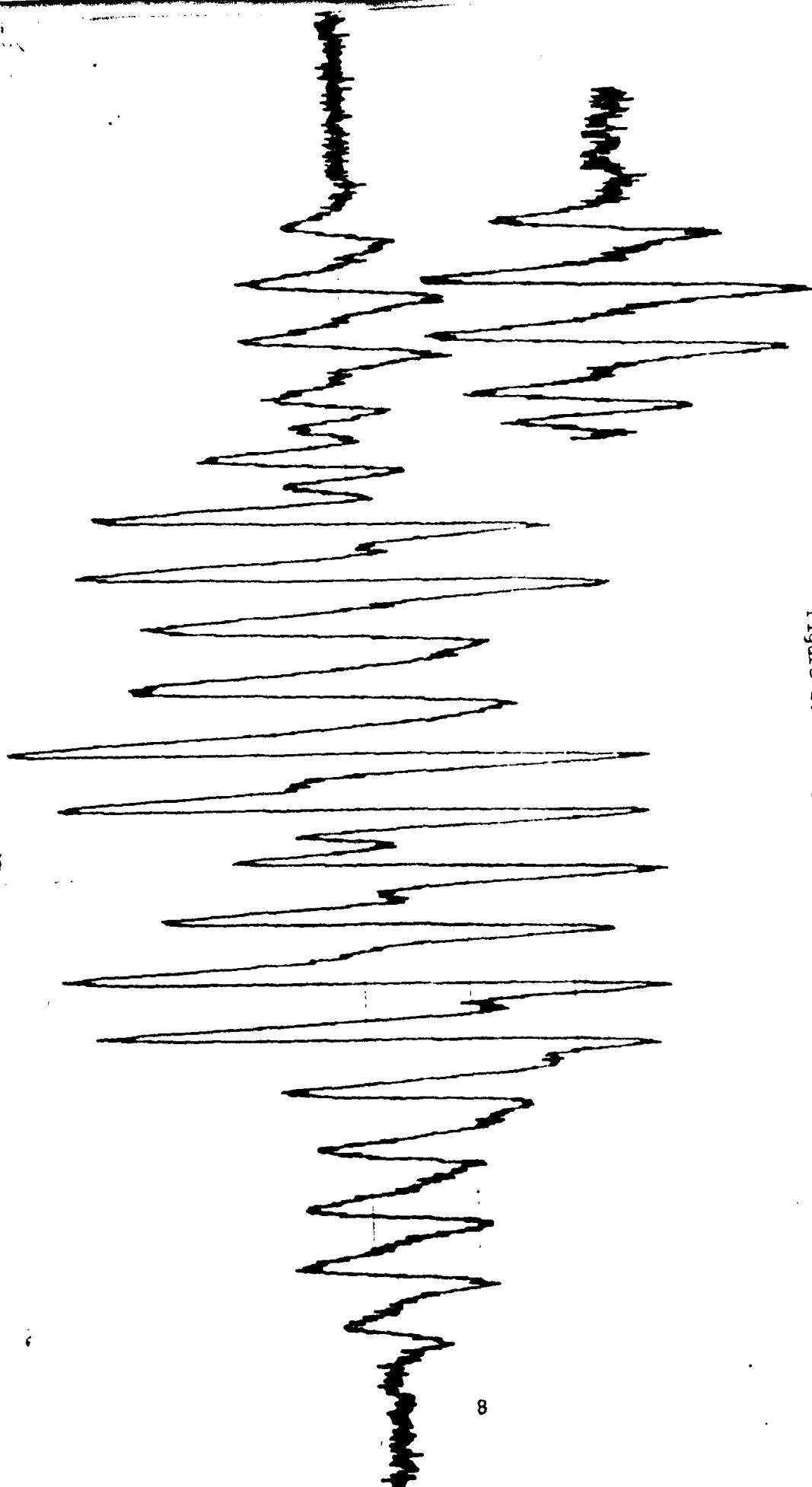


Figure 2: EPR Spectrum of DMBA Radical (b')

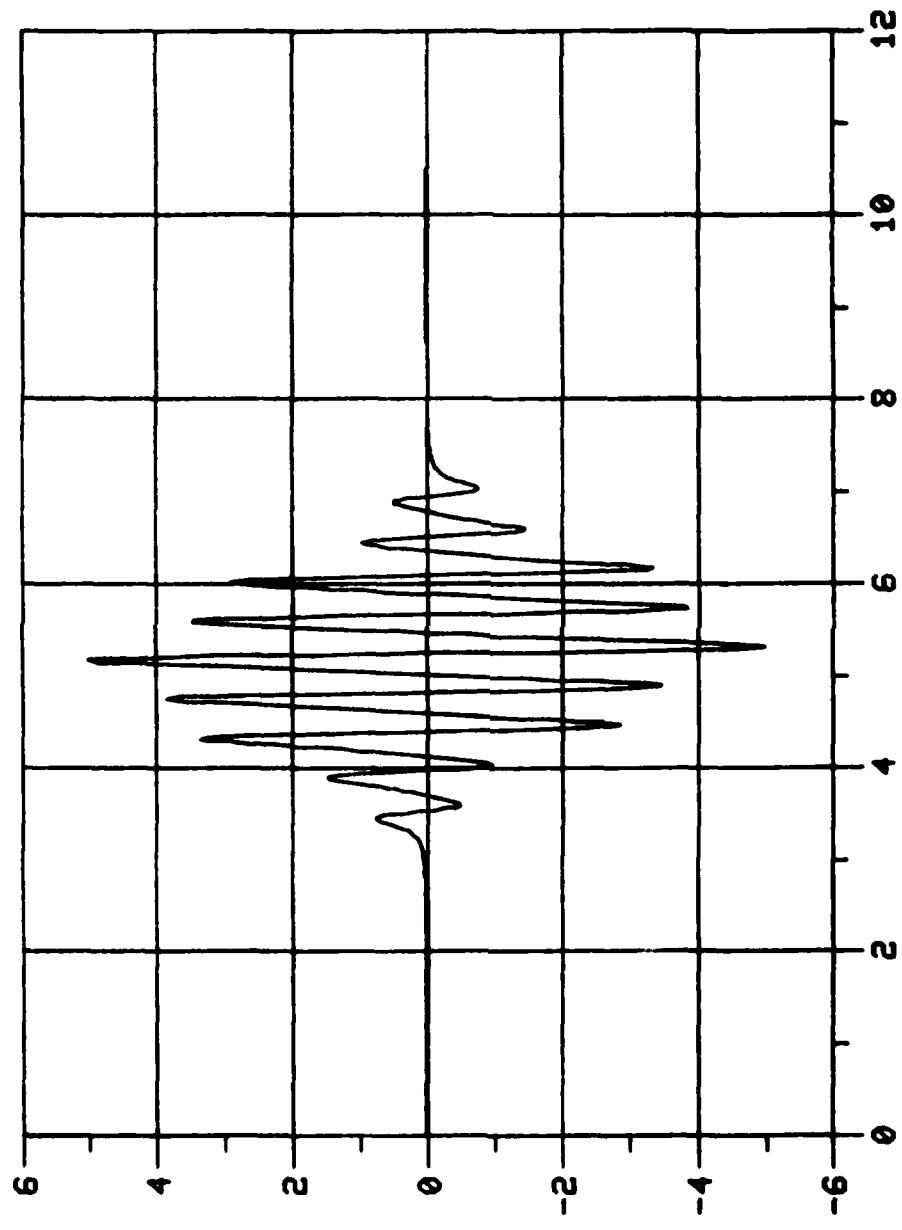


Figure 3: Simulated EPR Spectrum of Picramide Radical (a')

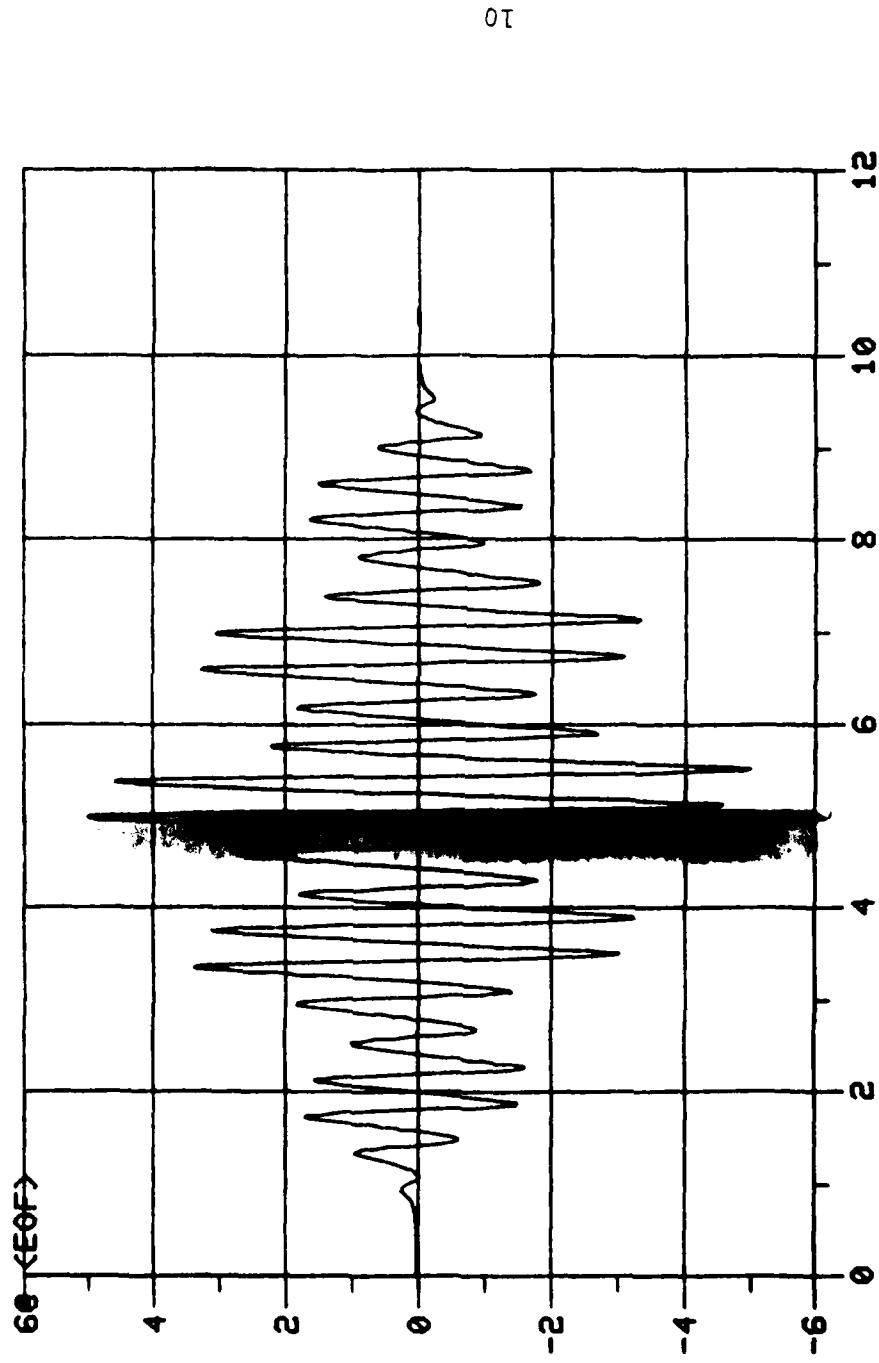
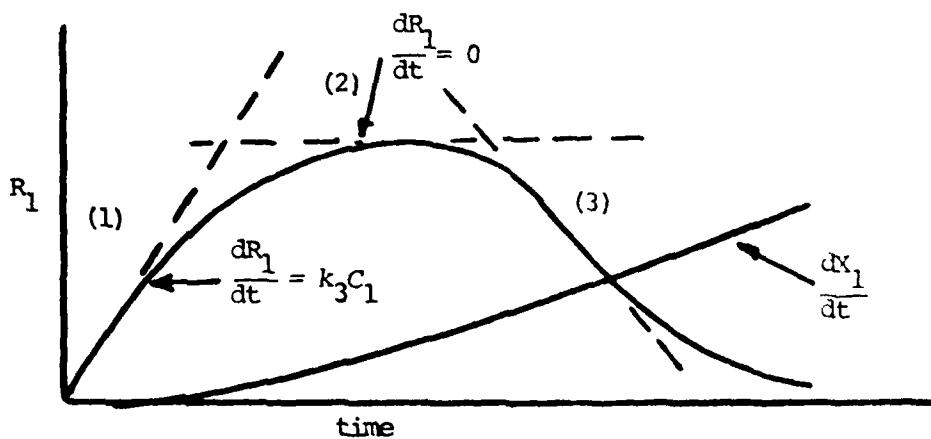
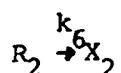


Figure 4: Simulated EPR Spectrum of ATB radical (b')

B. Kinetic Modeling. During the course of the thermal decomposition of TNT, picramide, DATB and other energetic materials, an intermediate radical is formed which later disappears. Subsequently, a radical signal develops which is associated with the development of a polymeric material. We have developed a general model for this thermal decomposition which is as follows:

#### HMB-EM RADICAL MECHANISM

In this model, HMB = hexamethylbenzene (or binder), EM = energetic material,  $R_1$  = intermediate radical,  $X_1$  = polymeric radical,  $R_2$  and  $X_2$  are presently undefined species.



The time factor indicates that  $C_1$  formation is very rapid relative to  $R_1$  formation. Phase (1) represents the formation of  $R_1$  from  $C_1$ . Phase (2)

represents the point at which the concentration of  $R_1$  is constant. Phase

(3) represents the loss of  $R_1$  to form the polymeric species,  $X_1$ .

As a result of a recent investigation of phase (1), the reaction of HMB with TNT has been shown to be 3/2 order in HMB. In a free radical mechanism, the presence of a 3/2 order term indicates that chain termination takes place between two radicals that undergo second order propagation reactions. We have derived three schemes which demonstrate this principle.

These mechanisms are one-half, first and three-halves order in EM, respectively.

Preliminary studies indicate that the mechanism is first order in TNT and three-halves order in HMB, as is the case with the last of the three proposed mechanisms.

Formation of  $R_1$  (intermediate radical):

Scheme (1)

(a)  $HMB + EM \xrightarrow{k_1} C$   
(b)  $C \xrightarrow{k_2} R^* + NO_2 + HMB^*$   
(c)  $R^* + C \xrightarrow{k_3} R_1 + C^*$   
(d)  $C^* \xrightarrow{k_4} R^* + HMB + NO_2$   
(e)  $2R^* \xrightarrow{k_5} Z$  (termination)

Steady-state assumptions:  $d(R^*)/dt = d(C^*)/dt = 0$

$$d(R^*)/dt = 0 = k_2 C - k_3 R^* C + k_4 C^* - k_5 (R^*)^2$$

$$d(C^*)/dt = 0 = k_3 R^* C - k_4 C^*$$

$$\Rightarrow k_4 C^* = k_3 R^* C$$

$$\Rightarrow k_5 (R^*)^2 = k_2 C \quad \Rightarrow R^* = (k_2 C / k_5)^{1/2}$$

$$d(R_1)/dt = k_3 R^* C = K' (HMB)^{3/2} (EM)^{3/2}$$

$$\text{where } K' = (k_1^{3/2} k_3^{1/2} k_2^{1/2}) / k_{-1}^{3/2} k_5^{1/2}$$

Scheme (2)

(a) see Scheme (1)  
(b) see Scheme (1)  
(c)  $R^* + HMB \xrightarrow{k_3} R_1 + HMB^*$   
(d)  $C + HMB^* \xrightarrow{k_4} R^* + Y + NO_2$   
(e)  $2R^* \xrightarrow{k_5} Z$  (termination)

Steady-state assumptions:  $d(R^*)/dt = d(HMB^*)/dt = 0$

$$d(R^*)/dt = 0 = k_2 C - k_3 R^* HMB + k_4 CHMB^* - k_5 (R^*)^2$$

$$d(HMB^*)/dt = 0 = k_2 C + k_3 R^* HMB - k_4 CHMB^*$$

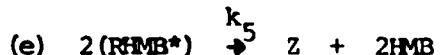
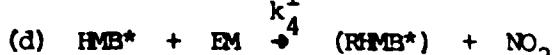
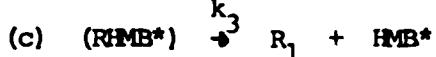
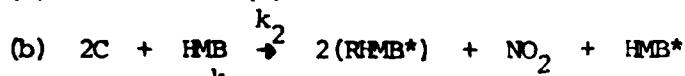
$$\Rightarrow k_5 (R^*)^2 = 2k_2 C; \Rightarrow R^* = (2k_2 C/k_5)^{1/2}$$

$$d(R_1)/dt = k_3 R^* HMB \\ = K' (HMB)^{3/2} (EM)^{1/2}$$

$$\text{where } K' = k_3 (2k_1 k_2 / k_{-1} k_5)^{1/2}$$

### Scheme (3)

(a) see Scheme (1)



Steady-state assumptions:  $d(HMB^*)/dt = d(RHMB^*)/dt = 0$

$$d(HMB^*)/dt = 0 = k_2 (HMB) C^2 + k_3 (RHMB^*) - k_4 (HMB^*) EM$$

$$d(RHMB^*)/dt = 0 = (1/2) k_2 C^2 HMB - k_3 (RHMB^*) + k_4 (HMB^*) (EM) - k_5 (RHMB^*)^2$$

$$\Rightarrow k_5 (RHMB^*)^2 = (3/2) k_2 C^2 (HMB)$$

$$d(R_1)/dt = k_3 (RHMB^*)$$

$$= K' (HMB)^{3/2} (EM)^{1/2}$$

$$\text{where } K' = (3k_2/2)^{1/2} (k_1/k_{-1})$$

C. Analysis of Activation Energies. The activation energies of the radical species  $a'$  and  $b'$ , are 41 and 44 kcal, respectively. These values are similar to those obtained in free radical reactions in which a carbon-nitrogen bond is broken. The EPR analysis of  $a'$  and  $b'$  along with recent evidence that the thermal decomposition of various energetic materials produces  $\text{NO}_2$ , suggests that the thermal decomposition of picramide and DATB involves the production of  $\text{NO}_2$ .

D. Use of TNB as a Complexing Agent and Binder. Our original proposal dealt with the use of TNB as a complexing agent and its general efficiency as a binder. Our observations are that thermal decomposition occurs more readily in TNT than in TNB. Consequently, we conclude that TNB would provide a longer shelflife than TNT, if used as a binding agent under comparable conditions.

E. Stop-flow Studies. The final part of our investigation dealt with stop-flow studies of DATB-TNB and picramide-TNB complexes. A stop-flow (Dionex) apparatus has been purchased and interfaced with a Biomation transient recorder, Tektronix scope and a recorder. We have just recently begun to obtain kinetic data on the proposed systems in acetonitrile. We will continue our investigation and extend it to include both TNB and TNT complexes, if this is feasible.

**III. List of Publications in Technical Journals:**

- A. EPR Studies of Thermochemical and Photochemical Decomposition of Nitramines in the Condensed Phase and in Solution, H. L. Pugh, L. P. Davis, J. S. Wilkes, W. R. Carper and R. C. Dorey, Proceedings of the Seventh International Symposium on Detonation (to be published)**
- B. First Steps of the Thermochemical Decomposition of Molten TNT, L. P. Davis, A. G. Turner, W. R. Carper, J. S. Wilkes, R. C. Dorey, H. L. Pugh and K. E. Siegenthaler, Thermochimica Acta(in preparation)**

**IV. Personnel Associated with the Project:**

**Dr. W. Robert Carper - Professor of Chemistry  
Mr. David P. Campbell - Ph.D. student in Chemistry**

**V. Interactions - Presented Papers:**

**See IIIB above - to be presented at the National A.C.S. meeting,  
Physical Chemistry Division, Atlanta, Ga., Mar. 28, 1981**

**VI. New Discoveries - Not applicable**

**VII. General Assessment:**

**The work accomplished under the auspices of this grant represents an important step forward in the development of a general model of the thermal decomposition of energetic materials. An understanding of both this phenomena and the overall effects of binders is crucial to the future development of improved methods in the areas of energetic material production and storage.**

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16. ABSTRACT (Continue on reverse side if necessary and identify by code letter) The thermal decomposition of picramide and DATB was monitored by electron paramagnetic resonance. Hexamethylbenzene and diethyl adipate were used as hosts. Radicals were formed whose composition was similar to the parent compound minus NO <sub>2</sub> . Thermal decomposition studies indicated an acceleration of picramide and DATB decomposition in TNT vs. TNB. A general mathematical model of thermal decomposition based upon binder complexation was developed. (over)			

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20. ABSTRACT (Cont'd)

In this model, complexation led to radical formation, followed by termination and polymerization steps. In addition, three general schemes of radical formation were derived, and one of these confirmed in preliminary experiments.

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